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Pathway Identification During Successful ISCR-Enhanced Bioremediation of a TCE DNAPL Source Area

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ABSTRACT: Groundwater at an active manufacturing facility on an 80-acre site in Portland, Oregon is impacted by TCE and its degradation products. Operations at the facility began in 1980, and included the use of TCE from approximately 1980 to 1989. TCE and/or TCE-containing wastewater were released to the subsurface in the early 1980s, roughly between 1980 and 1984. In 2006, concentrations of TCE and cis-1,2-dichloroethene (DCE) in the release area ranged as high as 592,000 and 90,000 ug/L (respectively) at depths ranging from approximately 50 to 110 ft (15 to 33 m) below ground surface (bgs). Based upon the source persistence and concentrations, it was presumed that TCE was present as a DNAPL.

Following bench and field pilot studies, ISCR-enhanced bioremediation was selected for source area treatment. Implementation consisted of an approximately 150 foot (46 m)-long permeable reactive barrier (PRB) consisting of EHC® and KB-1®. Monitoring data confirmed that the remedial action objective was achieved within six months following completion, with TCE below the MCL in several locations. Mass balance analysis suggests that ISCR-enhanced bioremediation treats the DNAPL by accelerated mass transfer from the non-aqueous phase to the dissolved phase, where TCE is rapidly converted to less toxic degradation products. The data suggest that this approach is a viable and practicable approach for *in situ* treatment of chlorinated solvent DNAPL source zones.

INTRODUCTION

Individually or in combination, *in situ* chemical reduction (ISCR) and enhanced anaerobic microbial degradation are recognized, well-established technologies for remediation of chlorinated solvent plumes downgradient of source areas. Chlorinated solvent DNAPL source areas are often treated with technologies that are resource-intensive (e.g., electric resistive heating), incompatible with operating facilities (e.g., removal), or unpredictable (e.g., surfactant flushing, neat or emulsified oil sequestration). ISCR and bioremediation have only recently been identified as likely viable technologies for chlorinated solvent DNAPL source zones (ITRC 2007). A brief sampling of the literature demonstrates how the current view has evolved since 2003, when the viability and practicality of DNAPL source zone remediation (regardless of method) was an open question (Kavanaugh et al., 2003). By coincidence, the technology screening, bench testing, field pilot testing, and full scale demonstration for this project have proceeded along a similar timeline, with the results in this paper indicating the viability of ISCR-enhanced bioremediation for chlorinated solvent DNAPL source zones.

Site description. The site is an operating facility in Portland, Oregon, adjacent to the Willamette River. Industrial operations at the facility began in 1980, after the site had been developed by filling during the 1970s. Industrial operations at the facility included the use of TCE from approximately 1980 to 1989. TCE and/or TCE-containing wastewater were released to the

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subsurface, roughly between 1980 and 1984, but the exact date and volumes are unknown. The releases likely occurred immediately upgradient of the primary manufacturing building, which covers most of the groundwater plume between the source area and the riverbank (Figure 1). Groundwater flows from the upland under the river, with a small portion of the impacted plume intersecting transition zone water and surface water in the river.

Figure 1. Site map and approximate extent of TCE in Groundwater.

Unlike some abandoned or inactive Brownfield sites, the source area at this site is located in the middle of an operating silicon wafer fabrication facility. During the initial technology screening, a variety of remedial technologies were evaluated and eventually discarded due to incompatibility with facility operations, or the presence of legacy MGP-related impacts. The technology screening left ISCR as the most viable DNAPL source removal technology. Subsequent comparative bench testing identified the combination of EHC® and KB-1® as the most efficient approach for treatment; these results were supported by subsequent field pilot testing, which in turn supported full scale implementation.

Implementation. Implementation consisted of an approximately 150 foot long PRB containing EHC and KB-1, installed at depths ranging from approximately 40 to 112 feet (12 to 34 m) bgs using direct-push technology. Supplemental injections were completed upgradient of the PRB to treat additional source areas. EHC was injected first, followed later (usually 7 to 14 days) by KB-1 injections. The EHC was injected at four-foot (1.2 m) vertical intervals, with two-foot (2.4 m) offsets between injection rows to enhance the vertical coverage.

Injections commenced in January 2009 and were completed in June 2009 (Cascade Drilling of Portland, Oregon). Approximately 200 injection points were completed as shown on Figure 2.

The EHC material was delivered to the site as a fine powder and mixed into a 30 percent slurry with potable water. The slurry was delivered to the subsurface using twin trailer-mounted ChemGrout 500a pumps powered by compressed air. EHC injections proceeded in a top-down fashion, using GeoProbe's pressure-activated injection tips. The KB-1 consortium was injected using a peristaltic pump and standard GeoProbe sampling screen and in a bottom-up fashion, using the same borings from the EHC injections.

In total, approximately 594,000 pounds (269,434 kg) of EHC and 1,831 liters of KB-1 (at a cell density of 1 x 10^{11} cells/L) were injected into the subsurface. The injection amounts were based on the successful field pilot test; however, based on the data presented below, these amounts may have been conservatively high and less materials could have been injected yielding similar results. Nevertheless, it is estimated that the longevity of the iron component of the EHC material will range from 14 to 21 years.

Groundwater data were collected from 23 wells located upgradient and within (Group 1), and downgradient (Group 2) of the PRB (Figure 2).

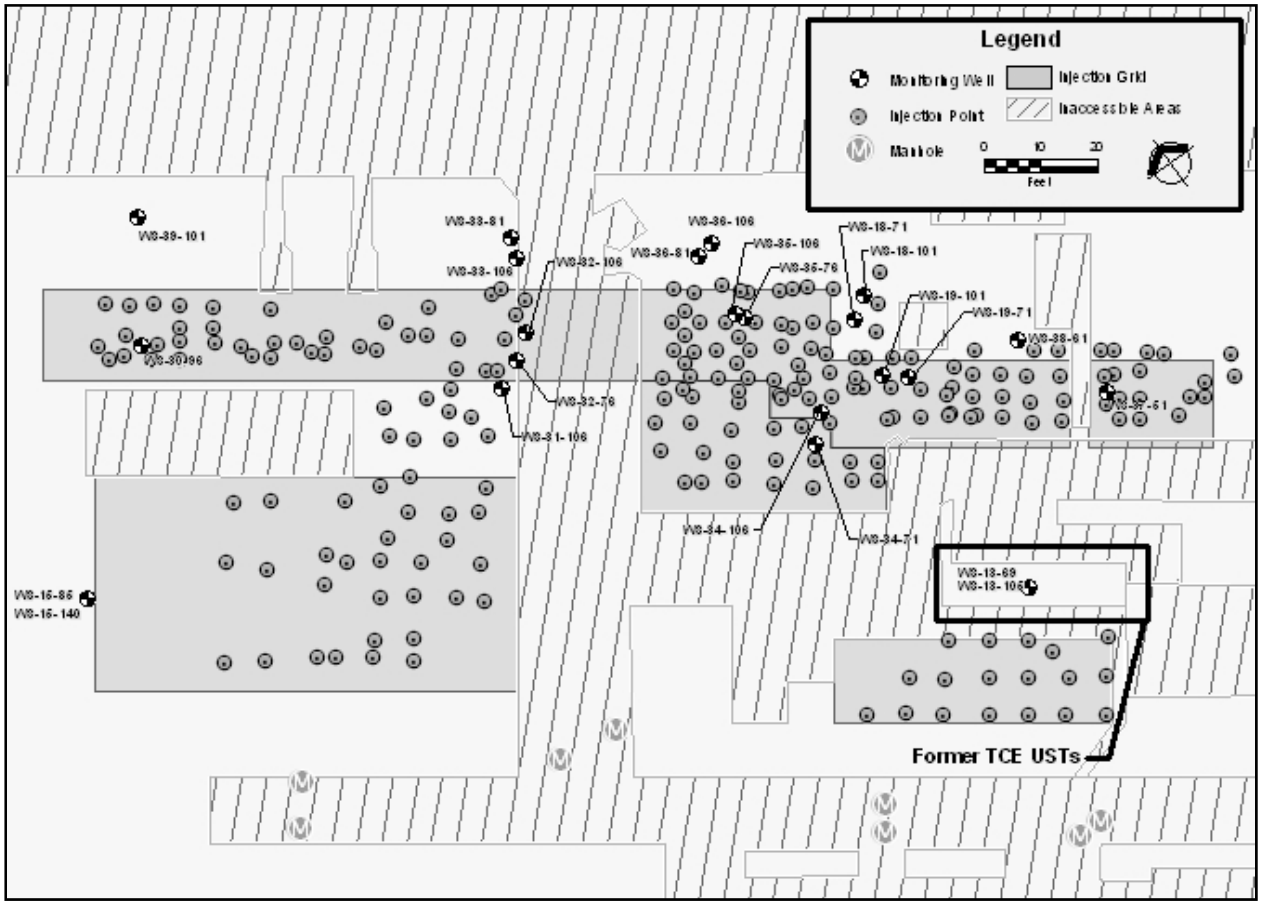

Figure 2. Injection layout

Eight wells pre-dated installation; the remaining wells were newly constructed per the request of the Oregon Department of Environmental Quality (DEQ). Data collection included an extensive suite of parameters to identify degradation rates and pathways. Target analytes

included TCE and its degradation products, including ethene, ethane, and chloride. Secondary analytes that confirmed distribution and/or migration of the injected materials included iron, total organic carbon, ketones, and Gene-Trac© analysis for KB-1 bacteria by SiREM.

METHODS

Data collected from January 2009 through January 2010 were used for the evaluation in this paper. The data evaluated included TCE and its degradation products, chloride, iron, and KB-1 bacteria counts. Changes in TCE concentrations relative to the remedial action objective (RAO; TCE below the 1 per cent of the solubility limit) and the federal maximum contaminant limit (MCL) were evaluated as the primary indicator of success. Mass conversion was estimated based upon changes in CVOC and chloride mass along transects oriented roughly transverse to the groundwater flow direction. Half-life values were estimated by modeling using first order trend fitting, and by simple regression of natural-log plots of concentrations.

RESULTS

The results indicate that ISCR-enhanced bioremediation was successful for TCE DNAPL removal; both biological and abiotic pathways are responsible for TCE mass removal; and TCE mass removal occurred at similar rates within and downgradient of the injection zone.

Progress toward RAO. TCE DNAPL was never directly observed in soil samples or monitoring wells. However, the combination of the high concentrations in reconnaissance samples and persistent high concentrations in a well located immediately below the former TCE storage area suggested a high probability that TCE DNAPL was present. Among other criteria, USEPA suggests that concentrations of chlorinated solvents in excess of 1 per cent of the aqueous solubility are indicative of the presence of DNAPL (USEPA, 1993). Based on this, the DEQ set the RAO as TCE concentrations below this threshold (11,000 ug/L).

Figure 3 is a log scatter plot of TCE concentrations. The data show that within six months following completion, the RAO was attained in all of the monitoring wells, demonstrating success. TCE concentrations in 10 monitoring wells were below 100 ug/L. TCE concentrations were below the federal MCL (5 ug/L) in another 10 monitoring wells. These data are very encouraging and demonstrate the viability of ISCR-enhanced bioremediation for TCE source areas.

Mass removal. The mass of TCE, cis-1,2-DCE, vinyl chloride, and chloride was estimated within the source area (defined where TCE exceeded 30 ug/L) and along three transects oriented transverse to the groundwater flow direction and within the estimated extents of the source area using the geostatistical estimating routines in the Environmental Visualization System (EVS) software program (developed by C-Tech; Laie, HI). Changes in TCE mass for the entire source area are summarized in Table 1. The data show that 98.2 per cent of the estimated TCE mass was removed within approximately six months following completion of the installation.

Table 1. Estimated TCE mass removal (kg)

Sampling Event	TCE Mass (kg)
2/17/2009	250
4/13/2009	90
6/30/2009 (end of injections)	40
7/28/2009	46
9/4/2009	25
10/28/2009	16
12/28/2009	4
Mass Reduction (kg)	245
% Mass Reduction	98.22

Table 2 summarizes changes in molar mass for TCE, cis-1,2-DCE and VC, and chloride in

the source area; summed for the three transects; and along the transect downgradient of Group 2 (Transect 3). The data show that daughter products were generated during the first half of 2009, but declined starting in about September 2009. The rapid decline resulted in a net loss of daughter products relative to the mass of TCE destroyed.

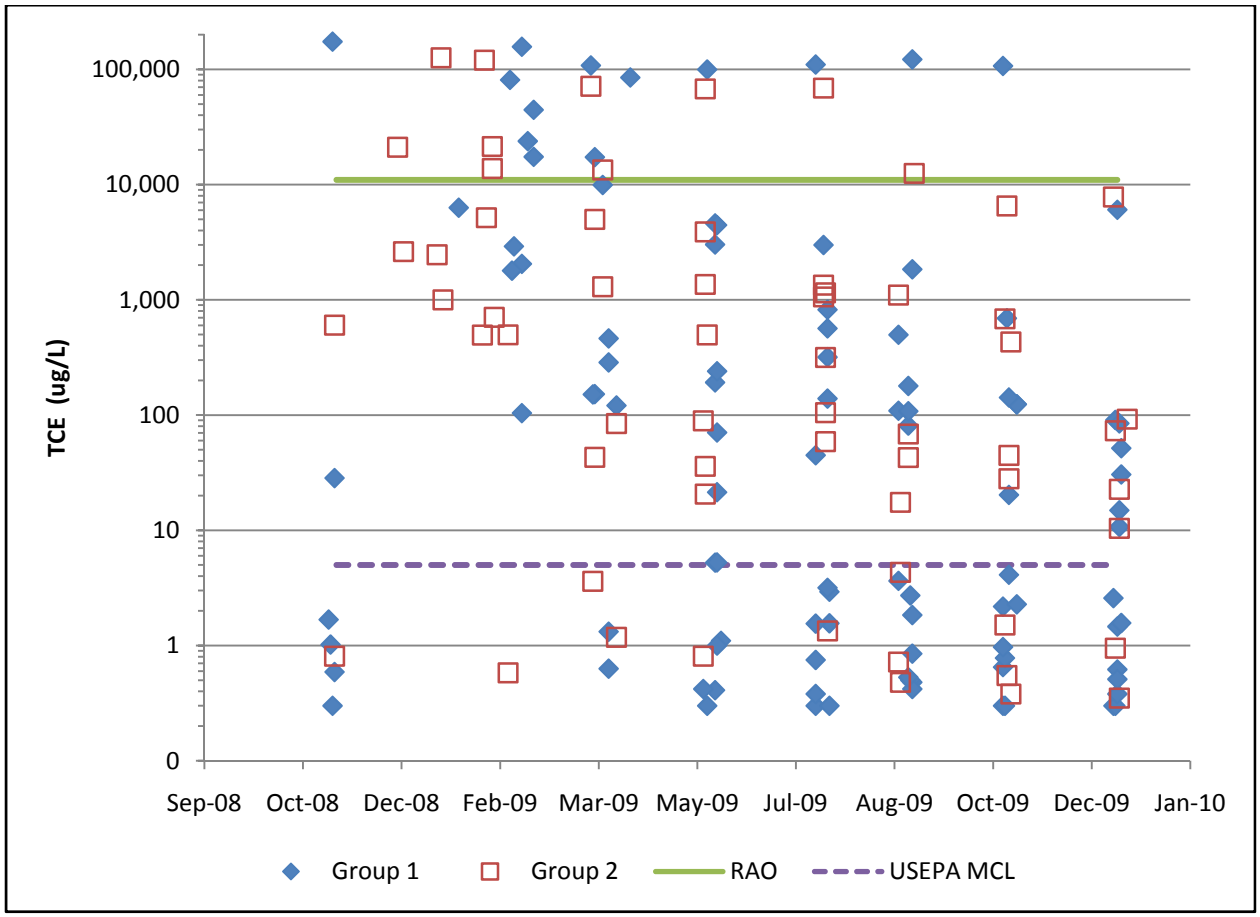

Figure 3. Log scatter plot of TCE in groundwater

The Transect 3 data show that mass destruction of TCE and its degradation products occurred within and downgradient of the injection zones, such that sustained increased concentrations of daughter products were not observed as a result of parent conversion.

The data also show that chloride generation was approximately 7x the amount of TCE destroyed, either within the source area or based upon the sum of the transects. The excess chloride in the dissolved phase suggests that excess mass of TCE was present, most likely as a DNAPL. Since EHC and KB-1 are primarily effective on dissolved-phase constituents, it follows that TCE DNAPL removal occurred as a function of accelerated dissolution from the non-aqueous phase.

Abiotic degradation products. Chloroalkane production via hydrogenation has been identified as a potential abiotic degradation pathway for TCE and its degradation products (Brown et al., 2009). 1,1,2-trichlorethane (1,1,2-TCA) was observed in the Group 1 wells (located under the former UST area) prior to the PRB installation, suggesting that some hydrogenation of TCE was occurring. Following the PRB installation, other chloroalkanes, specifically 1,1- and 1,2-dichloroethane (DCA) and chloroethane (CA), were observed at relatively low, but steady

concentrations. The DCA isomers were infrequently detected and at low concentrations (average of approximately 1 ug/L for both). CA was detected most frequently and at the highest average concentration of 17 ug/L. 1,1,2-TCA was often detected in the same wells where CA was detected but at lower average concentration (approximately 3 ug/L), suggesting that the hydrogenation pathway was producing both compounds, or that the sequential conversion of TCE to DCA and DCA to CA occurred at a relatively higher rate compared to the final conversion of CA to ethane. The low concentrations confirm that hydrogenation is occurring, but is not likely an important contributor to chloroalkene removal.

Table 2. Estimated mass removal (*M*)

Sampling Event	TCE Destroyed (*generated*)	DCE and VC Generated (*destroyed*)	Chloride Generated (*destroyed)*
Source Extents			
Apr-09	1,214	2,509	3,921
Jun-09	378	315	1,781
Jul-09	*(41)*	3,482	2,272
Sep-09	161	*(814)*	*(2,937)*
Oct-09	67	*(1,953)*	5,600
Dec-09	91	*(2,621)*	2,626
Totals (*M*)	1,870	918	13,263
Sum of Transects			
Apr-09	59	80	158
Jun-09	21	32	239
Jul-09	1	156	198
Sep-09	5	*(45)*	*(174)*
Oct-09	2	*(70)*	38
Dec-09	5	*(76)*	211
Totals (*M*)	93	76	669
Transect 3 (downgradient)			
Apr-09	8	31	48
Jun-09	2	1	135
Jul-09	*(2)*	30	80
Sep-09	3	*(45)*	*(126)*
Oct-09	0	*(7)*	207
Dec-09	0	*(42)*	68
Totals (*M*)	11	*(31)*	412

Abiotic trends. Abiotic degradation of chlorinated alkenes is characterized by simultaneous, as opposed to sequential dechlorination that is characteristic of microbial degradation (Brown et al., 2009). As indicated in Table 2, significant amounts of daughter products (primarily cis-1,2-DCE) were initially generated, in excess of the stoichiometry predicted by either abiotic or biologically-mediated pathways, indicating desorption and treatment of non-aqueous constituents (as DNAPL or sorbed to soil). Notwithstanding that TCE degradation via abiotic reductive dehalogenation results in cis-1,2-DCE generation at approximately 10 per cent by weight (via hydrogenolysis pathway), these data might argue against the abiotic pathway. However, simultaneous reductions in TCE and cis-1,2-DCE were observed in three locations, with similar slopes, as shown on Figure 4. These data provide an additional confirming line of evidence for abiotic degradation via beta-elimination.

Half-life data. Half-life data for TCE were calculated by two methods: simple slope calculations for the natural log of the concentration vs. time plots (the graphical method, which assumes first-order reaction), and least squares fitting using a first-order kinetic degradation model. The results of the graphical method generally matched the kinetic modeling, with half lives ranging from approximately 10 – 30 days independent of starting concentration. The agreement between the graphical method and good TCE curve fits from the model output (r^2 ~ 0.9 or better) indicate that degradation of TCE DNAPL follows a first-order reaction characteristic of both abiotic and biologically-mediated pathways.

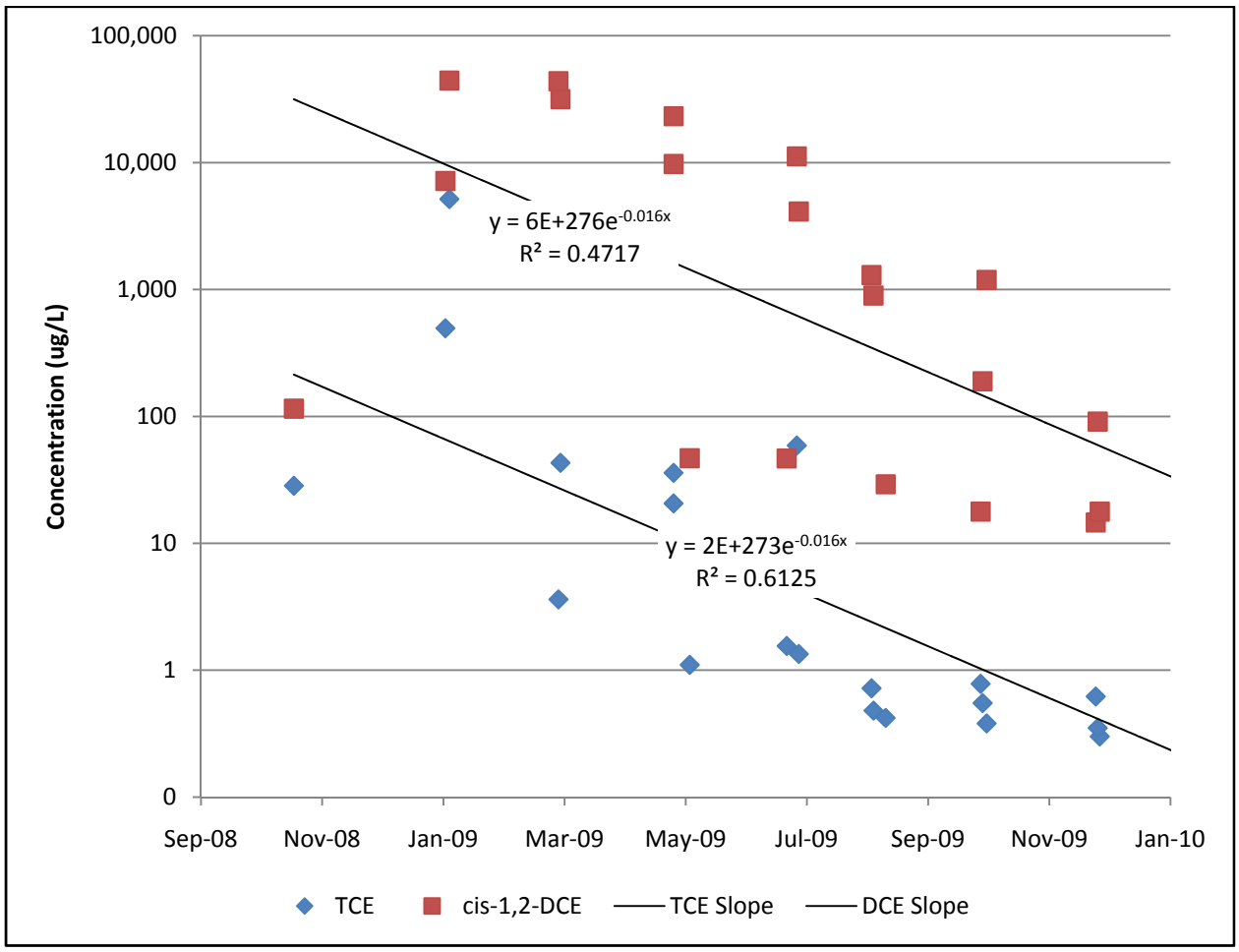

Figure 4. Simultaneous TCE and DCE trends suggesting abiotic degradation.

DISCUSSION

As is the case with many sites, the design of the full-scale implementation was constrained by site logistics and focused on achieving the RAO. In addition to clearly confirming the success of this approach, the fairly comprehensive data collection system yielded significant ancillary data to support analysis regarding the mechanisms for ISCR-enhanced bioremediation. Additional data, which were not described herein, included iron, ketones, and KB-1 concentrations which demonstrated the initial installation and advection downgradient of the remediation materials.

Initial groundwater concentrations and subsequent chloride data strongly suggest that TCE DNAPL was present, although not directly observed (as is often the case). Aqueous TCE concentrations declined rapidly, from well in excess of the 1 per cent solubility limit threshold, by two or three orders of magnitude. Assuming that EHC and KB-1 complete dechlorination in the aqueous phase, it appears that rapid TCE conversion in the aqueous phase creates a significant concentration gradient that accelerates mass transfer from the non-aqueous phase.

Research by others into ISCR has provided multiple lines of evidence that abiotic degradation of TCE can be an important removal mechanism. While this implementation was not

designed to rigorously evaluate this pathway, the data presented herein suggest several lines of evidence to indicate abiotic degradation of TCE and cis-1,2-DCE is occurring. This result is encouraging and indicates that further research is warranted.

Regardless of pathway, the data represent a very successful *in situ* TCE DNAPL source zone removal consistent with client and regulatory expectations. Industry opinion regarding the viability of *in situ* chemical remediation and or bioremediation for chlorinated solvent DNAPL source zones has evolved significantly during the last 10 years. Based on these data, ISCR-enhanced bioremediation represents a fairly flexible and relatively sustainable solution for what was previously viewed as an intractable problem.

SUMMARY

Groundwater data collected adjacent to an operating facility strongly indicated the presence of TCE DNAPL from approximately 40-110 feet bgs. Given a limited range of remedial options, initial bench testing was completed to compare ISCR and ISCR-enhanced bioremediation with other technologies, such as emulsified oil. The bench testing was follow by a field pilot, which suggested that full scale implementation would be successful.

EHC and KB-1 were injected to install a PRB across the source area, approximately 150 feet long. Installation required about six months. A comprehensive data collection network was sampled at the beginning of the installation, throughout installation, and for six months thereafter. Within five months following completion of the installation, TCE concentrations were below the RAO, in most wells below 100 ug/L, and below the MCL in about half of the wells.

The data show that TCE DNAPL mass was removed by accelerated partitioning to the dissolved phase, and multiple lines of evidence suggest that abiotic degradation of TCE and cis-1,2-DCE is occurring along with biologically-mediated sequential dechlorination. Comparison of half-life data estimated using different methods indicates that TCE removal is occurring as a first-order reaction. The data provided herein support previous predictions regarding the viability of ISCR and bioremediation for TCE DNAPL source zones.

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